PROPERTIES OF ETHYLENE OXIDE AND HYDRAZINE RELATED TO THEIR USE AS PROPELLANTS

Thesis by

William Clay Robison

1st Lt. USAF

In Partial Fulfillment of the Requirements

For the Degree of

Aeronautical Engineer

California Institute of Technology

Pasadena, California

1953

ACKNOWLEDGEMENTS

The author wishes to express his appreciation for many helpful discussions to Dr. S. S. Penner, under whose supervision this work was carried out. He also extends his thanks to Mr. Martin Goldsmith for help with experimental problems.

ABSTRACT

PART I. ETHYLENE OXIDE AS A MONOPROPELLANT

Thermodynamic calculations to determine the theoretical performance of ethylene oxide as a monopropellant have been carried out for various possible decomposition reactions. A survey of the literature on the kinetics of the thermal decomposition of ethylene oxide is presented.

PART II. EXPERIMENTAL MEASUREMENT OF THE HEATS OF DISSOCIATION OF HYDRAZINE - WATER AND HYDRAZINE - ALCOHOL SYSTEMS

A glass apparatus has been constructed for determining heats of dissociation at low temperatures. Published data on hydrazine-water mixtures have been checked. The heat of dissociation of $N_2H_4 \cdot CH_3OH$ has been found to be 8.62 Kcals/mole.

TABLE OF CONTENTS

PART I

ETHYLENE OXIDE AS A MONOPROPELLANT

I. INTRODUCTION

Ethylene oxide has been suggested as a useful monopropellant or gas generator. Considering the low adiabatic flame temperatures obtained, ethylene oxide appears to be an attractive monopropellant in spite of its relatively low performance. It is the purpose of the present discussion to summarize the expected performance of the monopropellant assuming various possible decomposition reactions (cf. Section II) and to review the available kinetic studies relating to the thermal decomposition of the monopropellant (cf. Section III).

Before proceeding with the discussion of the thermodynamics and kinetics of decomposition, it appears to be desirable to summarize the physico-chemical properties of ethylene oxide. Relevant data are given in Table I and are taken from a recent publication by Hess and Tilton[1].

Table I - Physical Properties of Ethylene Oxide

Liquid	
Reduced specific gravity, i.e., specific gravity at 20°C referred to water at 20°C.	.8711
Δ specific gravity / Δ temperature	$.00140(^{\circ}C)^{-1}$
Average weight at 20°C	$.8687 \frac{Kg}{liter}$
Coefficient of thermal expansion at 20°C	.00161
Coefficient of thermal expansion at 55°C	.00170
Boiling point at 1 atm.	10.7°C
Boiling point at .0658 atm.	-44°C

Table I - (Continued)

Liquid	
Boiling point at .0316 atm.	-66°C
Vapor pressure at 20°C	1.4408 atm.
Freezing point	-111.3°C
Refractive index, n_D, at 7°C	1.3597
Solubility in water at 10°C	Complete
Heat of vaporization at 1 atm.	5.996 Kcal / gram-mole

Vapor	
Vapor pressure at 20°C	1.4424 atm.
Critical temperature	195.8°C
Critical pressure	70.9657 atm.
Ignition temperature in air at 1 atm.	429°C
Auto ignition temperature at 1 atm.	571°C
Upper explosive limit in air at 1 atm.	100 o/o volume
Lower explosive limit in air at 1 atm.	3 o/o volume
Heat of Combustion, gross	308.7 Kcals / gram-mole
Heat of decomposition	20 Kcals / gram-mole

II. THERMODYNAMIC EVALUATION OF ETHYLENE OXIDE AS A MONOPROPELLANT

It is well known that reasonable upper limits on the performance of a chemical compound as a rocket propellant may be obtained by utilizing the equilibrium composition for a given reaction at the adiabatic flame temperature. In the case of ethylene oxide, however, the adiabatic flame temperature is so low that thermodynamic studies are not sufficient to determine the performance. The nature of the decomposition reaction is determined by chemical kinetics (cf. Section III). It is necessary to assume a particular type of decomposition reaction to calculate performance. The reaction which gives optimum performance can thus be determined and an attempt made to influence the mechanism of decomposition in order to obtain the most desirable reaction.

Four reactions by which ethylene oxide is known to decompose are listed below:

$$C_2H_4O(\ell) = CO + CH_4 - 26.02 \text{ kcal.} \qquad \text{(II-1)}$$

$$C_2H_4O(\ell) = CO + 2\,H_2 + C - 8.13 \text{ kcal.} \qquad \text{(II-2)}$$

$$C_2H_4O(\ell) = CO + 1/2\,C_2H_4 + H_2 - 1.88 \text{ kcal.} \qquad \text{(II-3)}$$

$$C_2H_4O(\ell) = CO + 1/2\,C_2H_2 + 3/2\,H_2 + 18.97 \text{ kcal.} \qquad \text{(II-4)}$$

In equations (II-1) to (II-4), heat evolved is identified by a negative sign. It is apparent from the heats of reaction that only equations (II-1) and (II-2) are of interest from a propellant performance standpoint. It is also clear that since the boiling point of ethylene oxide is 10.7°C, refrigeration will usually be necessary for liquid injection

into the rocket chamber.

The method described by Penner[2] will be followed here in calculating the performance corresponding to the decomposition reactions described by Eqs. (II-1) and (II-2). The simplifying assumptions involved are: thermodynamic equilibrium is reached in the combustion chamber after adiabatic reaction; the combustion products behave as ideal gases and expand adiabatically through the Laval nozzle; the expansion involves the one-dimensional flow of ideal, non-viscous gases, the gas velocity at the nozzle entrance is negligibly small as compared with that at the exit; no chemical reactions occur in the nozzle for the ethylene oxide monopropellant.

A. Performance Evaluation for the Reaction $C_2H_4O(\ell) = CO(g) + CH_4(g)$

If liquid ethylene oxide decomposes into gaseous carbon monoxide and gaseous methane, at constant pressure, the heat available, Q_{av}, is the heat of reaction, i.e.,

$$Q_{av} = \left[\Delta Hf(CO) + \Delta Hf(CH_4) - \Delta Hf(C_2H_4O)\right] = +(-26.42 - 17.89 + 18.29) = -26.02 \text{ kcal}, \qquad \text{(II-5)}$$

where the symbol ΔHf denotes the standard heat of formation. The heat absorbed, Q_c, at the chamber temperature, T_c, is then given by the relation

$$Q_c = \left[H(CO)_{T_c} - H(CO)_i\right] + \left[H(CH_4)_{T_c} - H(CH_4)_i\right] \qquad \text{(II-6)}$$

where H denotes an enthalpy. At T_c, $Q = Q_{av} + Q_c \equiv 0$. Assuming T_c to be $1400^\circ K$,

$$Q_c = (10.521 - 2.073) + (19.09 - 2.397) = 25.141 \text{ kcal}.$$

At $1500^\circ K$, $Q_c = (11.359 - 2.073) + (21.13 - 2.397) = 28.019$ kcal.

By linear interpolation, $T_c = 1430^{\circ}K$.

For frozen flow, the mole fractions, N, of the reaction products are $N_{CO} = 1/2$, $N_{CH_4} = 1/2$. The exhaust temperature, T_e, may be calculated by trial and error from the relation

$$N_{CO}\left[S(CO)_{T_c} - S(CO)_{T_e}\right] + N_{CH}\left[S(CH_4)_{T_c} - S(CH_4)_{T_e}\right] = R \ln(p_c/p_e) \tag{II-7}$$

where S denotes entropy and p is total pressure. Taking the chamber pressure, p_c, as 20.42 atmospheres and assuming ideal expansion to one atmosphere, it follows that $S(CO)_{T_e} + S(CH_4)_{T_e}$ = 115.33 cal/$^{\circ}$K-mole. At 900°K, $S(CO)_{T_e} + S(CH_4)_{T_e}$ = 112.74 cal/$^{\circ}$K-mole. Using linear interpolation it is found that $T_e = 908^{\circ}K$.

The average molecular weight of the gas mixture, M, is determined from the relation

$$M = N_{CO}M_{CO} + N_{CH_4}M_{CH_4} = 1/2(28) + 1/2(16) = 22 \text{ gm/mole.} \tag{II-8}$$

The molar enthalpy change, ΔH_c^e, is then

$$\Delta H_c^e = N_{CO}\left[H(CO)_{T_c} - H(CO)_{T_e}\right] + N_{CH_4}\left[H(CH_4)_{T_c} - H(CH_4)_{T_e}\right]$$
$$= 1/2(9.94 - 6.47) + 1/2(19.70 - 9.89) = 6.64 \text{ kcal/mole.} \tag{II-9}$$

The exit velocity, v_e, may be determined from the relation

$$1/2Mv_e^2 = \Delta H_c^e \tag{II-10}$$

whence $v_e = \left[(6640)(4184)/(11)\right]^{1/2} = 1590$ m/sec. For ideal expansion in a nozzle with a small divergence angle, the effective exhaust velocity, c, is approximately equal to the linear flow velocity, v_e. The specific impulse, I_{sp}, is

$$I_{sp} = c/g \simeq v_e/g = 1590/9,8 = 162.2 \text{ seconds.} \tag{II-11}$$

The average heat capacity ratio, δ , may be determined from the relation

$$T_e = T_c(p_e/p_c)^{[(\delta-1)/\delta]} \qquad \text{(II-12)}$$

whence it is found that $\delta = 1.18$. The characteristic velocity, c*, is defined by the relation

$$c^* = (1/\lambda)\,(RT_c/\delta M)^{1/2} = 1230\ \text{m/sec, where } \lambda = [2/(\delta+1)]^{[(\delta+1)/2(\delta-1)]} \qquad \text{(II-13)}$$

The thrust coefficient is

$$C_f = c/c^* = 1.295 \qquad \text{(II-14)}$$

B. Performance Evaluation for the Reaction:

$$C_2H_4O(\ell) = CO(g) + 2H_2(g) + C(c)$$

Here $Q_{av} = [\Delta Hf(CO) + 2\,\Delta Hf(H_2) + \Delta Hf(C) - \Delta Hf(C_2H_4O)]$ $= -8.13$ kcal. Also $Q_c = [H(CO)_{T_c} - H(CO)_i] + 2\,[H(H_2)_{T_c} - H(H_2)_i] + [H(C)_{T_c} - H(C)_i]$, and at 600°K, $Q_c = 7.168$ kcal whereas at 700°K, $Q_c = 9.714$ kcal. Using linear interpolation, it is found that $T_c = 638^\circ K$.

If the carbon is everywhere in temperature equilibrium with the gaseous products, the nozzle exit temperature may be determined from the relation $S(T_c) - S(T_e) = R \ln(p_c p_e)$, i.e.,

$$[N_{CO}S(CO)_{T_c} + N_{H_2}S(H_2)_{T_c} + N_C S(C)_{T_c}]$$
$$-[N_{CO}S(CO)_{T_e} + N_{H_2}S(H_2)_{T_e} + N_C S(C)_{T_e}]$$
$$= R \ln (p_c/p_e).$$

Thus $S(T_e)$ must be 37.13 cal/°K-mole. If $T_e = 400^\circ K$, $S(T_e) = 39.31$ cal/°K-mole, and if $T_e = 300^\circ K$, $S(T_e) = 37.05$ cal/K-mole. Using linear interpolation, the result $T_e = 304^\circ K$ is obtained.

The molar enthalpy change during expansion is $\Delta H_c^e = 2.742$ kcal. Also M = 14.67 g/mole; $v_e = c = 1250$ m/sec; $I_{sp} = 127.6$ seconds; $\delta = 1.326$; c* = 891 m/sec; and $C_f = c/c^* = 1.40$.

If the carbon is deposited in the rocket chamber, the heat capacity ratio for the gaseous mixture may be determined from the average heat capacity ratios of the products over the temperature interval T_c to T_e. For the temperature range between 638°K and 300°K: $C_{p_{av}}(H_2)$ = 6.973 cal/K-mole, $C_{p_{av}}(CO) = 7.080$ cal/K-mole, $C_p = (2/3)(1.973) + (1/3)(7.08) = 7.009$ cal/°K-mole, $C_v = C_p - R = 5.022$ cal/°K-mole. Also $\delta = 7.009/5.022 = 1.398$; $(T_c T_e) = (p_c p_e)^{[(\delta-1)/\delta]} = 2.36$; $T_e = 270$°K; $v_e^2 = 2C_p(T_c - T_e)/M$; M = 10.67 g/mole; $v_e = 1420$ m/sec; I_{sp} = thrust/(lb. of propellant/sec) = (exit mass flow x v_e)/(propellant mass flow x g) = 105.4 seconds. $C_f = \Gamma'\sqrt{[2/(\delta-1)]\,[1 - (p_e/p_c)^{[(\delta-1)/\delta]}]}$ where $\Gamma' = \delta[2/(\delta+1)]^{[(\delta+1)/2(\delta-1)]}$. $C_f = 1.385$. $c^* = C/C_f$ = 1025 m/sec.

Table II-1. Summary of Performance Calculations for C_2H_4O Monopropellant

Decomposition Reaction	T_c(K)	T_e(K)	c(m/sec)	c*(m/sec)	C_f	I_{sp}(sec)
$C_2H_4O = CO + CH_4$	1430	908	1590	1230	1.295	162.2
$C_2H_4O = CO + 2H_2 + C$ (carbon in equilibrium with gas)	638	304	1250	891	1.400	127.6
$C_2H_4O = CO + 2H_2 + C$ (carbon deposited in rocket chamber)	638	270	1420	1025	1.385	105.4

It is now clear that Eq. (II-1) gives optimum performance and that the occurrence of any other reaction will reduce performance considerably. The occurrence of reaction (II-2) would be particularly serious because of the operational difficulties connected with carbon formation. The factors leading to carbon formation in combustion processes are not clearly understood although recent papers by Porter[3] and Schalla[4] have shed some light upon the subject.

III. SURVEY OF PUBLISHED KINETIC STUDIES ON THE DECOMPOSITION OF ETHYLENE OXIDE

Since the kinetics of the thermal decomposition of ethylene oxide has not been studied in sufficient detail to permit a unique interpretation in terms of a reaction mechanism, the present survey is written as a historical review with emphasis on the observational data which led the author to postulate various plausible reaction mechanisms.

In 1926 Peytral [5] obtained the autodecomposition of ethylene oxide by passing it through a hot platinum tube. The reaction was exothermic and the reaction product contained water, acetaldehyde and a gas consisting of CO (44.7 %), H_2(28.3°/o), CH_4(15°/o), C_2H_2(5°/o), and C_4H_8(7°/o). Peytral accounted for the observed products by the following set of reactions.

Primary reactions:

$$4C_2H_4O \longrightarrow 4H_2CO + C_4H_8 \quad (56°/o), \qquad \text{(III-1)}$$

$$C_2H_4O \longrightarrow H_2O + C_2H_2 \quad (10°/o), \qquad \text{(III-2)}$$

$$C_2H_4O \longrightarrow CH_3CHO \quad (34°/o). \qquad \text{(III-3)}$$

Secondary reactions:

$$CH_3CHO \longrightarrow CO + CH_4, \qquad \text{(III-4)}$$

$$H_2CO \longrightarrow CO + H_2. \qquad \text{(III-5)}$$

$$C_2H_2 + H_2 \rightleftharpoons C_2H_4. \qquad \text{(III-6)}$$

Using the heats of reaction and the known speed with which the gas traversed the tube, Peytral estimated that, when rapid reaction began to occur, the temperature of the gases rose from about 571°C to 1200°C in about .002 seconds.

In 1929 Heckert and Mack[6] studied the slow decomposition of ethylene oxide between 380°C and 444°C in a pyrex chamber by measuring the total pressure as a function of time. They found the reaction to be homogeneous with carbon monoxide, methane, and hydrogen as products. The reaction exhibited a considerable induction period which ranged from 1-1/2 minutes at 444°C to 30 minutes at 380°C. A decrease in rate was noticed with decreasing initial pressure, but the pressure effect was not studied in detail. The effects of eleven diluents were studied. Ten of them, e.g., carbon dioxide, carbon monoxide, nitrogen, methane, ethane, propane, isobutane, argon, helium, and neon, depressed the rate, but hydrogen increased it considerably.

By postulating the reaction mechanism given below, Heckert and Mack were able to account for the induction period and the subsequently observed first order decomposition:

$$C_2H_4O \xrightarrow{k_1} B, \qquad \text{(III-7)}$$

$$B \xrightarrow{k_2} CH_4 + CO, \qquad \text{(III-8)}$$

where B is an intermediate formed during the thermal decomposition. Writing A for the concentration of C_2H_4O, C for that of CH_4, and D for that of CO, it is evident that

$$-d(A)/dt = k_1(A), \qquad \text{(III-9)}$$

$$-d(B)/dt = k_2(B) - k_1(A) \qquad \text{(III-10)}$$

$$+d(C)/dt = +d(D)/dt = k_2(B), \qquad \text{(III-11)}$$

where k_1 and k_2 denote, respectively, the specific reaction rate constants for the reactions described by Eqs. (III-7) and (III-8). Upon integration from $t = 0$ to the time $t = t$, and representing the initial

concentration of C_2H_4O by a, the following equation is obtained if the initial concentration C is zero:

$$(a - x)/a = \left[k_2/(k_2 - k_1)\right] \exp(-k_1 t) - \left[k_1/k_2 - k_1)\right] \exp(-k_2 t). \quad \text{(III-12)}$$

Here x denotes the concentration of reaction product C at time t. At the end of the induction period $t = t_2$ and $\left[k_1/(k_2-k_1)\right] \exp(-k_2 t_2)$ becomes negligibly small. Hence

$$(a-x_1)/(a-x_2) = \left[\exp(-k_1 t_1)\right] / \left[\exp(-k_1 t_2)\right] \quad \text{(III-13)}$$

whence

$$k_1 = \left[2.303/(t_2-t_1)\right] \log \left[(a-x_1)/(a-x_2)\right] . \quad \text{(III-14)}$$

For $t = t_2$ it is apparent from Eq. (III-12) that

$$(k_2 - k_1)/k_2 = 1 - (k_1/k_2) = \left[a/(a-x_2)\right] \exp(-k_1 t_2) \quad \text{(III-15)}$$

or

$$k_2 = k_1 y_2 / \left[y_2 - \exp(-k_1 t_2)\right]$$

where

$$y_2 = (a-x_2)/a.$$

The preceding equations were used to determine numerical values for the reaction rate constants k_2 and k_1. The result

$$k_1 = 9.95 \times 10^{-12} \exp(-52,000/RT) \text{ sec}^{-1} \quad \text{(III-16)}$$

was obtained. It should be noted that the reaction mechanism postulated by Heckert and Mack does not involve the intermediate production of free radicals.

Considerable theoretical discussion ensued over the experimental data obtained by Heckert and Mack who had suggested that the inter-

mediate B was a highly energized acetaldehyde molecule. They had reasoned that since the activation energy for the reaction was 52,000 calories and the heat of isomerization to the aldehyde was 23,000 calories, the energized molecule would have an excess energy of 75,000 calories. Kassel[7], however, pointed out that the value of k_1 at 380°C was .0025/sec, the half life of the intermediate therefore being about 280 seconds, and that it was unreasonable to suppose that activated molecules of acetaldehyde could retain excessive energy for so long a period of time.

Rice and Johnson[8] in 1934 studied the decomposition of ethylene oxide, ethane, dimethyl carbonate, propane, n-butane, n-heptane, n-pentane, acetone, acetaldehyde, ethyl alcohol, diethyl ether, dimethyl ether, trimethylamine, and dimethylamine into free radicals by utilizing the Paneth effect on metallic mirrors coated with antimony. Of the compounds studied, ethylene oxide was the least stable. This led Fletcher[9] to suggest that the ethylene oxide underwent two primary reactions, one, an isomerization to acetaldehyde, the other, a decomposition to give free radicals, and that the small amounts of free radicals catalyzed the decomposition of the aldehyde by a chain mechanism. Sickmann[10], using the assumption that a third body was necessary for the recombination of free radicals, treated Fletcher's premise mathematically. His reaction scheme was as follows, where R represents any free radical:

$$C_2H_4O \xrightarrow{k_1} 2R, \qquad \text{(III-17)}$$

$$C_2H_4O \xrightarrow{k_1'} CH_3CHO. \qquad \text{(III-18)}$$

$$R + CH_3CHO \xrightarrow{k2} RH + CO + R, \qquad \text{(III-19)}$$

$$2R + (M) \xrightarrow{k_4} X + (M). \qquad \text{(III-20)}$$

Here X is a stable molecule formed from the two free radicals R. Representing the concentration of C_2H_4O by c_1, that of R by c_2, and that of CH_3CHO by y, he wrote the steady state equation for the free radical concentration as;

$$dc_2/dt = 2k_1 c_1 - 2k_4 c_2^2 = 0, \qquad \text{(III-21)}$$

or

$$c_2 = \sqrt{(k_1 c_1/k_4)} \qquad \text{(III-22)}$$

where $k_4 = k_4'(M)$. The rate of disappearance of ethylene oxide was written as

$$-dc_1/dt = k_1 c_1 + k_1' c_1 = k c_1 \qquad \text{(III-23)}$$

where $k = k_1 + k_1' \simeq k_1'$ if $k_1 \ll k_1'$. The concentration of C_2H_4 at any time is then

$$c_1 = A \exp(-kt) \qquad \text{(III-24)}$$

where A is the initial concentration of C_2H_4O. The net rate of formation of acetaldehyde becomes

$$dy/dt = k_1' c_1 - k_2 c_2 y = k_1' c_1 - k_2 \sqrt{(k_1 c_1/k_4)}\, y$$

$$= k_1' A \exp(-kt) - k_2 \sqrt{(k_1 A/k_4)}\, [\exp(-kt/2)]\, y. \qquad \text{(III-25)}$$

Setting $\exp(-kt/2) = x$, which maps the t-axis from 0 to ∞ on the x-axis from 1 to 0, Eq. (III-25) becomes

$$dy/dx = -2k_1' Ax/k + 2k_2 y \sqrt{(k_1 A/k_4)}/k = -Qx + Py \qquad \text{(III-26)}$$

where $P = 2k_2 \sqrt{(k_1 A/k_4)}/k$ and $q = 2k_1' A/k \simeq 2A$. Integration of

Eq. (III-26) between x and 1, remembering that at $t = 0$, $x = 1$ and $y = 0$, gives the concentration of the aldehyde, viz.,

$$y = Q/P \left\{1 + Px - (1 + P) \exp \left[-P(1 - x)\right]\right\} \qquad \text{(III-27)}$$

The quantity P was evaluated for Heckert and Mack's data as about 160.

In 1936 Thompson and Meissner [11, 12] measured the rate of decomposition between 435°C and 505°C using methods generally similar to those used in the work by Heckert and Mack[6]. Their results agreed quite well with the previous data. It was noticed, however, that the total pressure increase for complete reaction fell below 100°/o at higher temperatures or pressures, the minimum value being slightly less than 80°/o at their highest temperature 505°C. This was explained as the result of a polymerization process occurring simultaneously with the decomposition. A dark, solid product was formed at high temperatures which subsequently decomposed slowly. Segmentation (i.e., discontinuities) of the plot of time of half-change versus initial pressure was obtained. At 475°C, the period of half-change was almost independent of initial pressure when the latter was greater than 250 mm. There was a bimolecular region between 40 mm and 250 mm and at least one other such region below 40 mm. The activation energy was calculated as 53,000 cals/mole at 400 mm and 50,000 cals/mole at 50 mm. A reaction mechanism was not suggested. It is interesting to note the very slight dependence of activation energy on total pressure.

Also in 1936 Fletcher and Rollefson [13] reinvestigated the decomposition of ethylene oxide as well as its effect as a catalyst upon

the decomposition of acetaldehyde. Their experimental data also agreed with those of Heckert and Mack[6]. They suggested that the ethylene oxide partly decomposes to formaldehyde and partially isomerizes to acetaldehyde:

$$C_2H_4O \xrightarrow{k_1} HCHO + CH_2, \qquad \text{(III-28)}$$

$$C_2H_4O \xrightarrow{k_2} CH_3CHO. \qquad \text{(III-29)}$$

Since no methylene radicals were detected, they suggested that these reacted very rapidly with ethylene oxide to produce methyl radicals which would cause a chain decomposition:

$$CH_2 + C_2H_4O \xrightarrow{k_3} 2\,CH_3 + CO, \qquad \text{(III-30)}$$

$$CH_3 + CH_3CHO \xrightarrow{k_4} CH_3 + CH_4 + CO. \qquad \text{(III-31)}$$

The methyl radicals could be removed by direct recombination or in the presence of a third body:

$$2\,CH_3 \xrightarrow{k_5} C_2H_6, \qquad \text{(III-32)}$$

$$2\,CH_3 + M \xrightarrow{k_6} C_2H_6 + M. \qquad \text{(III-33)}$$

Taking x_1 as the pressure of ethylene oxide, x_2 as that of the methylene radicals, x_3 as that of the acetaldehyde, x_4 as that of the methyl radicals, P as the total pressure, and assuming reaction (III-28) to be first order, they obtained the following result:

$$x_4 = \sqrt{(2k_3x_1x_2)/(k_5 + k_6P)} = \sqrt{(2k_1x_1)/(k_5 + k_6P)}. \qquad \text{(III-34)}$$

They assumed $k_2 > k_1$ since the ratio of formaldehyde detected to

acetaldehyde detected was small and the amount of hydrogen found in the products was only 7 °/o of the total. Taking Eq. (III-31) as the main reaction they wrote

$$dP/dt \sim k_4 x_4 x_3 \sim k_4 x_3 \sqrt{(2k_1 x_1)/(k_5 + k_6 P)}. \qquad \text{(III-35)}$$

When acetaldehyde pressure reaches a maximum, x_3', at an early stage of decomposition, $x_1 \simeq P_o$ and at this time t_{max}:

$$k_2 P_o = k_4 x_4 x_3' \qquad \text{(III-36)}$$

Then

$$x_3' = (k_2 p_o)/k_4 \sqrt{(k_5 + k_6 P/(2k_1 p_1)} \qquad \text{(III-37)}$$

or

$$dP/dt_{max} \sim k_2 P_o. \qquad \text{(III-38)}$$

They pointed out that dP/dt_{max} was actually proportional to a higher power of the concentration of ethylene oxide than the first. Inert gases, which help to maintain the Maxwell-Boltzmann distribution of activated molecules, may slightly increase dP/dt_{max}. Inert gases which contribute to the total pressure or remove free radicals should increase the maximum amount of aldehyde and therefore t_{max}. These possibilities are in agreement with the data of Heckert and Mack. Fletcher and Rollefson suggested however that since nitric oxide did not change dP/dt_{max}, only the induced decomposition of acetaldehyde and not the isomerization was a chain reaction. From the product analysis, they calculated that 14 °/o of the ethylene oxide decomposed into free radicals. They found the induced decomposition of acetaldehyde to vary with the square root of the ethylene oxide concentration and with slightly less than the

first power of the aldehyde concentration. Using this rate, they calculated the amount of the aldehyde that should be present if the ethylene oxide all isomerized to acetaldehyde and compared it with the amount actually found. For a pressure of 380 mm at 441°C, the observed value was 8.8 mm and the calculated value 11 mm.

Thompson and Meissner[14] in a later work with another alkene oxide, propylene oxide, found its decomposition to be essentially parallel with that of ethylene oxide. They studied the effects of nitric oxide on both decompositions and found the rates of both to be slightly depressed. They pointed out that acetaldehyde is not decomposed by nitric oxide whereas propionaldehyde is affected slightly, and that a greater difference should have been observed if the primary reaction was an isomerization to an aldehyde.

An experiment in 1948 using infrared spectrometry[15] showed good agreement with the earlier data. The rates obtained from the spectrometer data agreed with those obtained by total pressure methods provided that the latter were based upon the actual rather than the theoretical ratio of initial to final pressure. Maximum concentrations of $H_2C{:}C{:}O$ and of acetaldehyde occurred at approximately one quarter of the reaction time. Formaldehyde was not detected although concentrations up to 1 % could not be excluded. The experiment was not suitable for the detection of free radicals. The proportion of CO, C_2H_6, and C_3H_8 in the reaction products remained relatively constant throughout the reaction while the proportion of CH_4 increased and that of H_2 decreased.

Recent studies by Burden and Burgoyne[16] upon the ignition limits of ethylene oxide reveal that nitrogen has no lowering effect upon the ignition pressure of the pure gas. This would support the premise that the decomposition is not a chain reaction. They suggest that the decomposition proceeds by a quasiunimolecular collision reaction having the total effect of the following equations:

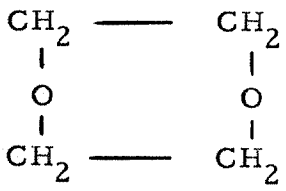
$$C_2H_4O \longrightarrow CH_4 + CO, \tag{III-39}$$

$$2\,C_2H_4O \longrightarrow C_2H_4 + 2\,CO + 2\,H_2. \tag{III-40}$$

An energetic collision between two molecules of ethylene oxide could result in a short lived complex which may revert to the original two molecules or decompose by either of two paths:

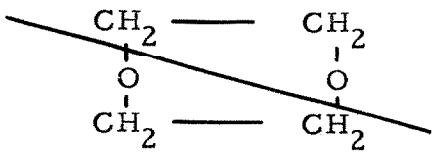
$$2\,C_2H_4O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_2H_4O)_2 \begin{cases} \xrightarrow{k_3} 2\,CH_4 + 2\,CO \\ \xrightarrow{k_4} C_2H_4 + 2\,CO + H_2 \end{cases} \tag{III-41}$$

Burden and Burgoyne suggest as an illustrative example the structure of the intermediate as



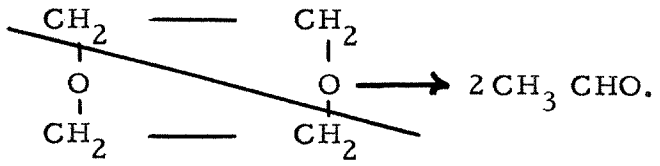
Then there are three possible modes of decomposition:

(1) Collision with another molecule leading to scission



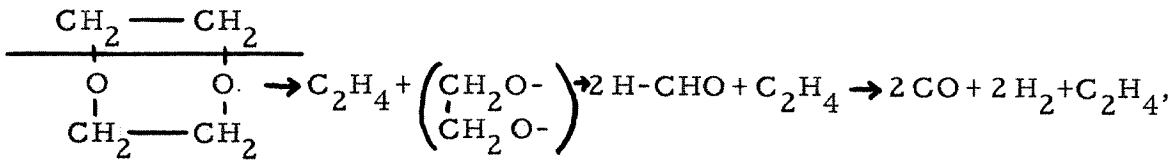
and subsequent reformation of ethylene oxide.

(2) A spontaneous scission of the same type leading to the exothermic formation of acetaldehyde



The exothermic effect of the isomerization of ethylene oxide to acetaldehyde would be sufficient to initiate the decomposition of the aldehyde to CO and CH_4.

(3) A scission



Mueller and Walters [17] using standard chemical procedures have attempted to determine the fraction of ethylene oxide disappearing by free radical reaction. The influence of methyl radicals was studied by adding mercury dimethyl to the ethylene oxide. Their results indicated that the radicals could react with the ethylene oxide but that the average chain length was not large. The decomposition of mercury dimethyl is itself a complex reaction and, therefore, little could be told about the rate of production of the methyl radicals. The effect of propylene upon the decomposition of ethylene oxide was studied also, and it was found that the normal rate of decomposition of ethylene oxide was reduced by approximately one-half when the ratio of propylene to ethylene oxide was .5. There seemed to be no induction period in the rate of disappearance of the pure ethylene oxide. Mueller

and Walters suggested that a large part of the decomposition proceeded by the reaction:

$$CH_3 + C_2H_4O \longrightarrow CH_4 + C_2H_3O \qquad \text{(III-42)}$$

The fate of the C_2H_3O radical as well as the analyses of the intermediate products was to be presented in a further publication, which has not yet appeared.

III A. CONCLUSIONS

In spite of the fact that a great deal of experimental work has been done on the kinetics of thermal decomposition of ethylene oxide, it is clear that our knowledge has not progressed to the point where it is possible to predict the exact course of the decomposition reaction in a gas-generating unit or in a rocket motor chamber. For this reason, additional experimental studies, concerning particularly the effect of metal catalysts on the course of the reaction, appear to be indicated. Preliminary studies along these lines were performed by using the glass apparatus described in Part II. However, no useful results were obtained with nickel and aluminum catalysts because it was not possible to perform measurements at sufficiently high temperatures.

PART II

EXPERIMENTAL MEASUREMENT OF THE HEATS OF DISSOCIATION OF HYDRAZINE - WATER AND HYDRAZINE - ALCOHOL SYSTEMS

I. INTRODUCTION AND SUMMARY

Altman and Adelman[18] have determined that gaseous hydrazine hydrate exists only as a monohydrate in the temperature and pressure range $5^{\circ}C < T < 90^{\circ}C$ and $2 < P < 10$ mm. They studied the equilibrium between hydrazine and water in the vapor phase by following the pressure change in a constant volume apparatus and found the heat of dissociation of hydrazine hydrate to be 13.97 Kcal/mole. Their data on hydrazine hydrate have been checked. Furthermore, the heat of dissociation of $N_2H_4 \cdot CH_3OH$ has been determined and was found to be 8.62 Kcal/mole.

II. APPARATUS

A constant volume apparatus was constructed to study the heats of dissociation of $N_2H_4 \cdot H_2O$ and $N_2H_4 \cdot CH_3OH$. The apparatus consisted essentially of a pyrex flask immersed in an oil bath. The vapor to be studied was introduced into the flask, the temperature systematically changed, and after sufficient time had elapsed for equilibrium to occur at each temperature, the pressure was recorded.

A sketch of the experimental arrangement is shown in Figure 1. A Cenco-Megovac pump was used to evacuate the system. Pressure measurements were made with a Wallace-Tiernan manometer, which is

accurate to ± 0.1 mm. of mercury. A Fenwal thermo-regulator switch was used with a calrod type immersion heater to control the temperature of the bath. A stirrer driven by a small electric motor was used to minimize temperature gradients in the bath. High vacuum hose was used to connect the manometer to the all-glass reaction vessel; high vacuum stopcock lubricant and glyptal were used to prevent leakage of air into the apparatus.

III. EXPERIMENTAL PROCEDURE

The flask was thoroughly cleaned with sulfuric acid-dichromate solution, and then washed five times with tap water and five times with distilled water. An equimolar mixture of $N_2H_4 \cdot H_2O$ or $N_2H_4 \cdot CH_3OH$ was prepared from 98 °/o pure hydrazine and placed in a 200 ml. flask. After assembling all components of the apparatus, the system was evacuated to a pressure of less than one millimeter of mercury. The apparatus was considered to be leak proof when a pressure increase of less than one millimeter occurred over a period of several hours.

The system was flushed several times with the hydrazine hydrate or alcoholate vapor to minimize the amount of atmospheric oxygen remaining adsorbed on the glass walls. The vapor was then introduced and the equilibrium pressures recorded as a function of temperature. The manometer was kept evacuated, except during actual readings, in order to minimize chemical reaction between the hydrazine-hydrate or alcoholate vapor and the mercury or rubber hose. It was found that the volume of gas outside of the flask during a representative run was 2 °/o of the total volume. The apparatus was allowed to return to room

temperature after each experimental run in order to recheck the equilibrium pressures and to make certain that no irreversible decomposition reactions had occurred. Since deviations of the gases from ideality were negligible under the experimental conditions, and since no thermal decomposition occurred, it may be concluded that the deviation of the measured pressure at a given temperature from the calculated perfect gas pressure was produced by the dissociation of the hydrazine-hydrate or alcoholate to hydrazine and water or to hydrazine and methyl alcohol.

Using the standard methods,[18] the partial pressure of each chemical species at equilibrium was calculated as follows. The decomposition reactions are:

$$N_2H_4 \cdot H_2O(g) = N_2H_4(g) + H_2O(g) \qquad \text{(III-1)}$$

$$N_2H_4 \cdot CH_3OH(g) = N_2H_4(g) + CH_3OH(g) \qquad \text{(III-2)}$$

We may symbolize Eqs. (III-1) and (III-2) as

$$HX \rightleftharpoons H + X. \qquad \text{(III-3)}$$

Let P_T = total pressure at any time;

P_i = total pressure if no dissociation of the HX occurred subsequent to the filling operation;

P_o = total pressure of the gases, assuming complete dissociation;

y = mole fraction of HX decomposed

= mole fraction of H present

= mole fraction of X present.

Assuming ideal mixtures of the gases, it is apparent that:

$$P_{HX} = P_i (1 - y) \tag{III-4}$$

$$P_{H} = P_X = P_i\, y \tag{III-5}$$

$$P_i = P_o/2 \tag{III-6}$$

$$P_T = P_i(1 - y) + 2P_i\, y = P_i (1 + y) \tag{III-7}$$

From Eq. (III-7)

$$y = \frac{P_T}{1/2\, P_o} - 1 = \frac{P_T - 1/2\, P_o}{1/2\, P_o}, \tag{III-8}$$

$$1 - y = 1 - \frac{P_T}{1/2\, P_o} + 1 = \frac{P_o - P_T}{1/2\, P_o} \tag{III-9}$$

The equilibrium constant K_p is given by the relation

$$K_P = \frac{(P_i\, y)^2}{P_i (1 - y)} = \frac{P_i\, y^2}{1 - y} = \frac{(P_T - 1/2\, P_o)^2}{P_o - P_T} \tag{III-10}$$

It is apparent that the equilibrium constant depends only on P_o and P_T. At the higher temperatures, where dissociation is practically complete, $P_T = P_o = nRT/V$. The perfect gas curve may be extrapolated to the lower temperature to give the hypothetical values of P_o occurring in Eq. (III-10) in the region of partial dissociation. The heat of dissociation may then be determined from the slope of the curve for log K_p as a function of the reciprocal of the absolute temperature.

IV. EXPERIMENTAL RESULTS

Figures 2 and 3 show graphs of log K_p plotted versus the reciprocal of the absolute temperature for $N_2H_4 \cdot H_2O$ and $N_2H_4 \cdot CH_3OH$, respectively. The curves form fairly straight lines in the temperature

range covered.

The heat of dissociation (Δ H) of $N_2H_4 \cdot H_2O$, as determined from the relation $\Delta H = - R \, d\ln K_p / d(1/T)$, is 14.34 Kcal/mole for the curve shown in Figure 2. This checks reasonably well with the value of 13.97 Kcal/mole determined by Altman and Adelman.[18] The heat of dissociation for $N_2H_4 \cdot CH_3OH$, as determined from the slope of the curve in Figure 4, is 8.62 Kcal/mole. This value may be taken as the standard heat of dissociation, $\Delta H^{o}_{2\,98}$, since the temperatures covered by the experiments are not too far above 298°K. The standard heat of formation (ΔHf) of $N_2H_4 \cdot CH_3OH$ may then be determined from the heats of formation of CH_3OH (g) and N_2H_4(g) and from the heat of dissociation. In this manner it is found that

Δ Hf $[N_2H_4 \cdot CH_3OH(g)]$ = 22.75 - 162.47 - 8.62 = 148.34 Kcal/mole.

REFERENCES

1. L. V. Hess and V. V. Tilton, Ind. and Eng. Chem. 42, 1251 (1950)
2. S. S. Penner, Am. Journ. Phys. 20, 26, (1952)
3. G. Porter, 4th Symposium on Combustion, Abstracts of Papers, p. 35, M.I.T., (Sept. 1952)
4. R. G. Schalla, and G. E. McDonald, NACA RM E 52I22, (Dec. 1952)
5. E. Peytral, Bull. Soc. Chem. 39 , 206 (1926)
6. W. H. Heckert, and E. Mack, J. Am. Chem. Soc. 51, 2706 (1929)
7. L. S. Kassel, Homogeneous Gas Reactions, p. 284, The Chemical Catalogue Co. (1932)
8. F. O. Rice, and W. R. Johnson, J. Am. Chem. Soc. 56, 214 (1934)
9. G. J. M. Fletcher, J. Am. Chem. Soc. 56, 214 (1934)
10. D. J. Sickman, J. Chem. Phys. 4, 297 (1936)
11. H. W. Thompson, and M. Meissner, Nature 137, 870 (1936)
12. H. W. Thompson, and M. Meissner, Trans. Faraday Soc. 34, 1222 (1938)
13. C. J. M. Fletcher, and G. K. Rollefson, J. Am. Chem. Soc. 58, 2135 (1936)
14. H. W. Thompson, and M. Meissner, Trans. Faraday Soc. 34, 1222 (1938
15. G. L. Simard, J. Steger, T. Mariner, D. J. Salley, and V. Z. Williams, J. Chem. Phys. 16, 836 (1948)
16. J. H. Burgoyne, and F. A. Burden, Proc. Roy. Soc. (London) 199A, 328 (1949)
17. K. H. Mueller, and W. D. Walters, J. Am. Chem. Soc. 73, 1458 (1951)
18. D. Altman, and B. Adelman, J. Am. Chem. Soc. 74, 3742 (1952)
19. National Bureau of Standards, Tables of Selected Values of Chemical Thermodynamic Properties, Series III, Vol. I, March 31, 1947 to June 30, 1949

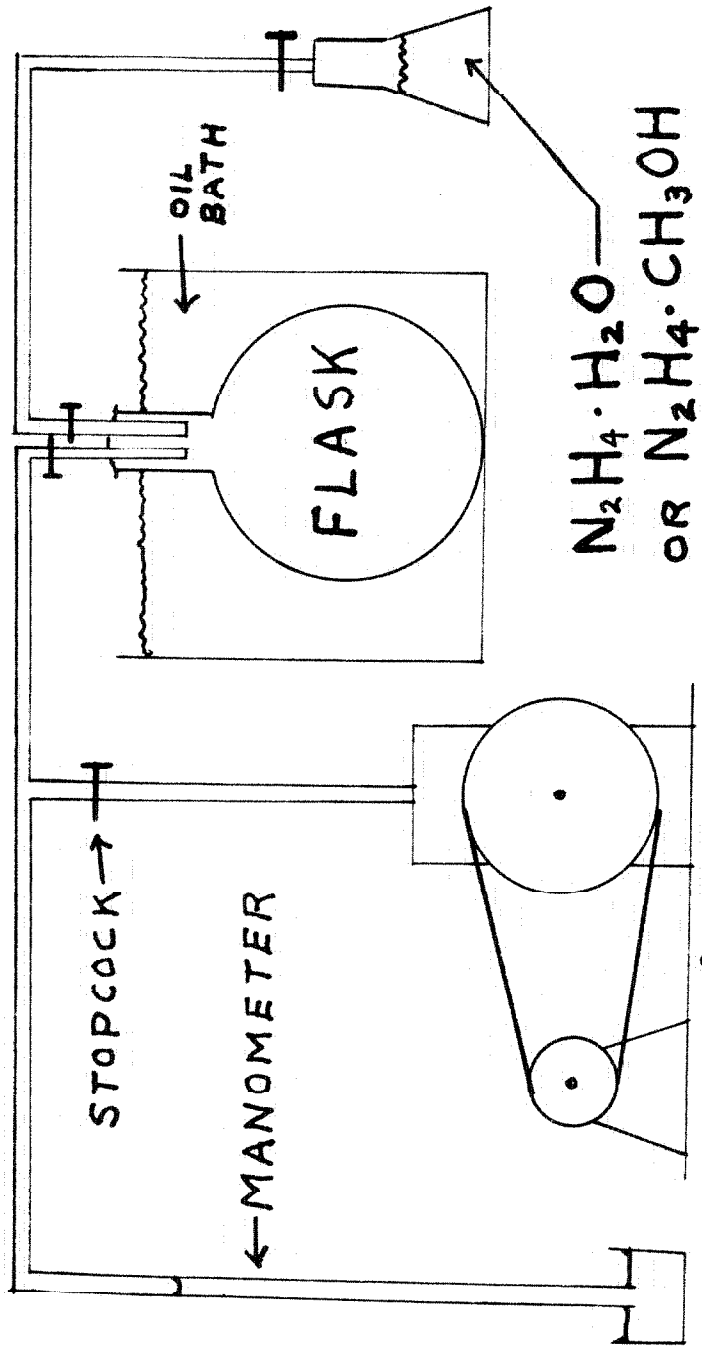


FIGURE 1 - EXPERIMENTAL ARRANGEMENT

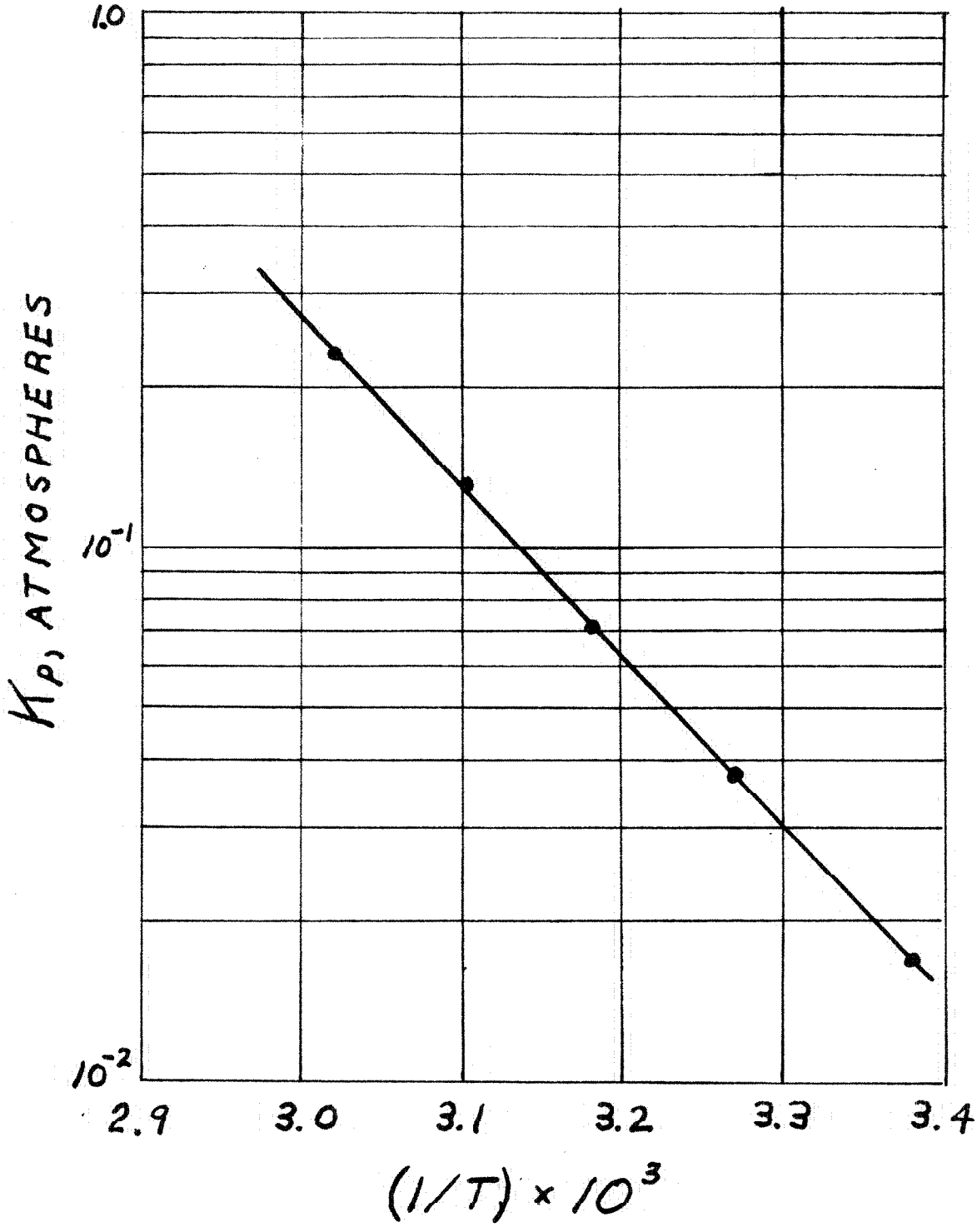


FIGURE 2

DISSOCIATION OF $N_2H_4 \cdot H_2O$

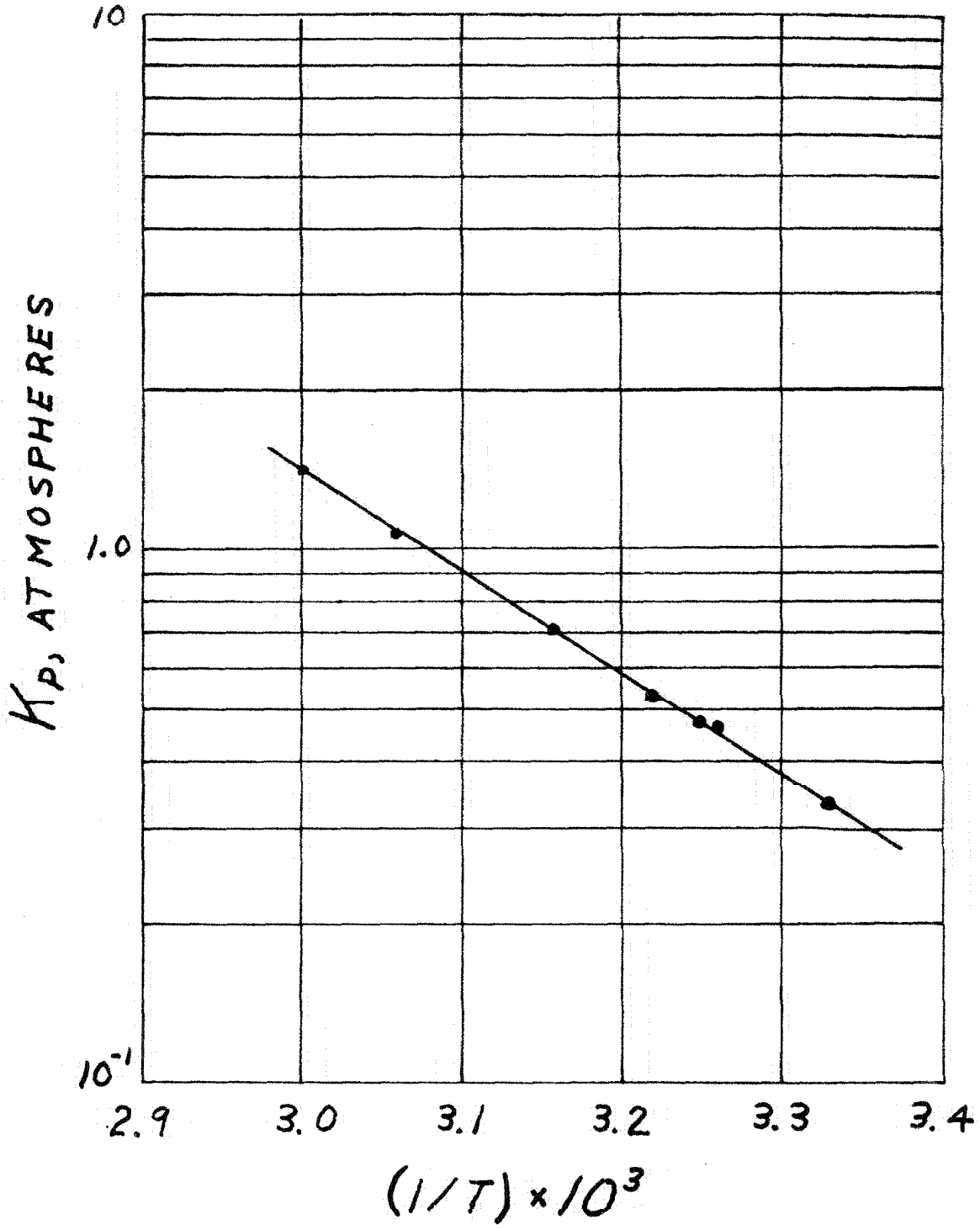


FIGURE 3

DISSOCIATION OF $N_2H_4 \cdot CH_3OH$